

## SPECIFICATION

### RUBBER MASTER BATCH AND PRODUCTION METHOD THEREOF

#### TECHNICAL FIELD

[0001] This invention relates to a rubber master batch and a method for producing the same, a rubber composition using the rubber master batch, and a tire and a belt using the rubber composition, and more particularly to a method for producing a rubber master batch having an excellent homogeneity.

#### BACKGROUND ART

[0002] Heretofore, the use of a rubber-filler wet master batch (a rubber master batch) is known as a production method of a rubber composition having an excellent processability. In this case, the rubber master batch is obtained by mixing a rubber solution with a slurry obtained by previously mixing a filler such as carbon black, silica or the like with water at a certain ratio and finely dispersing the filler into the water by a mechanical force, then coagulating the resulting mixture by adding a coagulating agent such as an acid, an inorganic salt, an amine or the like, collecting the coagulated mass through filtration and drying it (see JP-B-36-22729 and JP-B-51-43851).

[0003] Among the above rubber master batches, a rubber master batch using styrene-butadiene copolymer rubber (SBR) latex as the rubber solution has been already produced on a commercial scale and is widely used. However, a rubber master batch using a rubber latex having high coagulating property such as a natural rubber latex or the like as the rubber solution is not yet industrialized because the coagulation reaction starts at the step of mixing the rubber solution with the filler slurry before the addition of the coagulating agent and hence (i) it is difficult to stir the mixture homogeneously and the homogeneity of the coagulated mixture is bad, or (ii) it is difficult to control a coagulation state.

[0004] On the other hand, JP-A-2000-507892 discloses a method for producing a rubber master batch without adding the coagulating agent and an example using the natural rubber latex as the rubber solution. However, this method requires a special equipment for introducing the  
5 filler slurry into the latex flow at a high speed, and hence there is a problem that the large-scale equipment investment is required.

[0005] Also, EP-A-1283219 discloses a method for producing a rubber master batch using a natural rubber latex in which an amide bond is decomposed, but the homogeneity of the resulting rubber  
10 master batch is not studied. In this literature, as the method for mixing the natural rubber latex with the filler slurry are mentioned a method wherein the filler slurry is charged into a homomixer and the latex is added dropwise with stirring, and a method wherein the filler slurry is added dropwise to the latex with stirring.

15 SUMMARY OF THE INVENTION

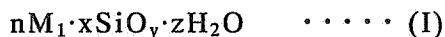
[0006] It is, therefore, an object of the invention to solve the above-mentioned problems of the conventional techniques and to provide a method for producing a rubber master batch capable of producing the rubber master batch having an excellent homogeneity without  
20 requiring the special equipment. Furthermore, it is another object of the invention to provide a rubber master batch obtained by the method, a rubber composition using the rubber master batch, and a tire and a belt using the rubber composition.

[0007] The inventors have made various studies in order to achieve  
25 the above objects and discovered that the rubber master batch having an excellent homogeneity can be obtained by mixing the rubber solution with the filler slurry by means of a static mixer or a high shear mixer, and as a result the invention has been accomplished.

[0008] That is, the method for producing the rubber master batch  
30 according to the invention is a method for producing a rubber master batch comprising a step of mixing a rubber solution with a slurry solution of a filler previously dispersed into a liquid, characterized in that a static mixer or a high shear mixer comprising a rotor and a

stator portion is used in the mixing of the rubber solution and the slurry solution. Also, the rubber master batch of the invention is produced by this method.

[0009] In the method for producing the rubber master batch  
5 according to the invention, it is preferable that the filler is at least one selected from the group consisting of carbon black, silica and an inorganic filler represented by the following formula (I):



wherein  $M_1$  is at least one selected from the group consisting of a  
10 metal of aluminum, magnesium, titanium, calcium or zirconium, oxides and hydroxides of these metals, their hydrates, and carbonates of these metals,  $n$  is an integer of 1-5,  $x$  is an integer of 0-10,  $y$  is an integer of 2-5, and  $z$  is an integer of 0-10.

[0010] In a preferable embodiment of the method for producing the  
15 rubber master batch according to the invention, the rubber solution is a water-based rubber latex. In this case, it is more preferable that the rubber latex is a natural rubber latex. Furthermore, the natural rubber latex is particularly preferable that an amide bond in the latex is decomposed with a protease.

20 [0011] In another preferable embodiment of the method for producing the rubber master batch according to the invention, the water-based rubber latex is mixed with the slurry solution, and the resulting mixture is coagulated to have a water content of 5-40 mass%, and the coagulated mass is dried while applying a mechanical shearing  
25 force. In this case, it is more preferable that the drying is performed by a screw-type continuous kneader.

[0012] Furthermore, the rubber composition of the invention is characterized by compounding the rubber master batch obtained by the above-described method. The rubber composition may be preferably  
30 used in a tire and a belt.

[0013] According to the method for producing the rubber master batch of the invention, the rubber master batch having an excellent homogeneity can be produced without the special equipment.

## BEST MODE FOR CARRYING OUT THE INVENTION

[0014] The invention will be described in detail below.

The method for producing the rubber master batch according to the invention comprises a step of mixing the rubber solution and the slurry  
5 solution of the filler previously dispersed into the liquid, and is characterized in that the static mixer or the high shear mixer comprising the rotor and the stator portion is used in the mixing of the rubber solution and the slurry solution at the step, and does not need the special equipment. Also, the rubber master batch of the invention  
10 is obtained by this method and is very high in the homogeneity.

[0015] When the static mixer is used in the mixing step, it is considered that since the static mixer has not a driving portion, a shearing force is hardly applied to the mixture, and also even if the coagulation is partially caused, since the resulting coagulated mass has  
15 a structure of hardly causing the clogging, the mixing can be carried out homogeneously while maintaining a good productivity. Therefore, the resulting rubber master batch is excellent in the homogeneity.

[0016] On the other hand, when the high shear mixer is used in the mixing step, it is considered that the homogeneity of the resulting  
20 rubber master batch as a whole is improved because even if the rubber solution and the filler slurry are coagulated inhomogeneously, the coagulated mass is crushed finely by the high shearing force.

[0017] The static mixer used in the production method of the invention is a static-type mixing machine having no driving portion,  
25 and is referred to as a motionless mixer. In the static mixer, fluid is sequentially agitated and mixed by fixed elements, and a size of dispersed particles becomes smaller every the pass through the element. The static mixer is a common mixer, and for example, commercially available products supplied by Noritake Co., Limited, TAH Company  
30 in USA, KOFLO Company in USA, TOKUSHU KIKI KOGYO Co., Ltd. and so on can be used.

[0018] On the other hand, the high shear mixer used in the production method of the invention comprises the rotating rotor and

the fixed stator portion. In the high shear mixer, the rotor rotating at a high speed and the fixed stator portion are arranged at a narrow clearance, and a high shearing force is produced by the rotation of the rotor. At this point, the high shearing means a shear speed of not less than 2000/s and is preferable to be not less than 4000/s. As the high shear mixer can be used commercially available products. For example, a homomixer made by TOKUSHU KIKI KOGYO Co., Ltd., a colloid mill made by PUC Company in Germany, high shear mixers made by CAVITRON Company in Germany and SILVERSON Company in UK and so on can be used preferably.

[0019] As the rubber solution are mentioned a rubber latex in which particles of a rubber component are dispersed in the water and a solution in which the rubber component is dissolved in an organic solvent. As the rubber component are mentioned natural rubber (NR) as well as synthetic diene-based rubbers such as styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), chloroprene rubber (CR) and the like. They may be used alone or in a combination of two or more. The concentration of the rubber component in the rubber solution is preferably 5-60 mass%, more preferably 10-40 mass%.

[0020] As the rubber solution, water-based rubber latexes are preferable. Among these rubber latexes, natural rubber latex is particularly preferable. According to the method of the invention, even if the water-based latex of natural rubber or the like easily causing coagulation is used, the resulting rubber master batch is high in the homogeneity owing to the above-mentioned reasons. In case of using the natural rubber latex, the resulting rubber master batch is excellent in the mechanical properties, low heat build-up and wear resistance.

[0021] In the natural rubber latex, an amide bond in the latex may be decomposed with a protease (a protein-splitting enzyme). By decomposing the amide bond in the natural rubber latex can be suppressed entwinement of molecules due to hydrogen bond of the

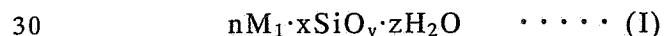
amide bond to control the rise of the viscosity of rubber and to improve the processability.

[0022] The protease has a nature of hydrolyzing the amide bond existing in a surface layer component of the natural rubber latex particles, and includes, for example, an acidic protease, a neutral  
5 protease, an alkaline protease and so on. In the production method of the invention, the alkaline protease is particularly preferable in view of the effects.

[0023] When the amide bond is decomposed with the protease, such  
10 a decomposing treatment may be performed under a condition suitable for the enzyme to be mixed. For example, when Alkalase 2.5L type DX made by NOVOZYMES is mixed with the natural rubber latex, it is preferable to usually conduct the treatment within a temperature range of 20-80°C. In this case, pH is usually adjusted to a range of  
15 6.0-12.0. Also, the amount of the protease added is usually a range of 0.01-2 mass%, preferably a range of 0.02-1 mass% based on the natural rubber latex.

[0024] In the step of decomposing the amide bond in the natural rubber latex, it is also preferable to add a surfactant for improving the  
20 stability of the latex. As the surfactant can be used an anionic surfactant, a cationic surfactant, a nonionic surfactant and an amphoteric surfactant, and among them the anionic surfactant and the nonionic surfactant are particularly preferable. The amount of the surfactant added can be properly adjusted in accordance with the nature  
25 of the natural rubber latex, but is usually a range of 0.01-2 mass%, preferably a range of 0.02-1 mass% based on the natural rubber latex.

[0025] The slurry solution is formed by previously dispersing the filler into the liquid. As the filler are mentioned carbon black, silica and an inorganic filler represented by the following formula (I):



wherein  $M_1$  is at least one selected from the group consisting of a metal of aluminum, magnesium, titanium, calcium or zirconium, oxides and hydroxides of these metals, their hydrates, and carbonates

of these metals, n is an integer of 1-5, x is an integer of 0-10, y is an integer of 2-5, and z is an integer of 0-10.

[0026] As the carbon black are mentioned various grades of carbon black such as SAF, HAF, ISAF, FEF, GPF and the like. As the silica  
5 are mentioned precipitated silica, fumed silica, colloidal silica and so on. As the inorganic filler represented by the formula (I) are mentioned alumina ( $\text{Al}_2\text{O}_3$ ) such as  $\gamma$ -alumina,  $\alpha$ -alumina or the like; alumina monohydrate ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) such as boehmite, diaspore or the like; aluminum hydroxide [ $\text{Al}(\text{OH})_3$ ] such as gibbsite, bayerite or the  
10 like; aluminum carbonate [ $\text{Al}_2(\text{CO}_3)_3$ ], magnesium hydroxide [ $\text{Mg}(\text{OH})_2$ ], magnesium oxide ( $\text{MgO}$ ), magnesium carbonate ( $\text{MgCO}_3$ ), talc ( $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ ), attapulgite ( $5\text{MgO} \cdot 8\text{SiO}_2 \cdot 9\text{H}_2\text{O}$ ), titanium white ( $\text{TiO}_2$ ), titanium black ( $\text{TiO}_{2n-1}$ ), calcium oxide ( $\text{CaO}$ ), calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ], aluminum magnesium oxide ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ), clay  
15 ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), kaolin ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), pyrophyllite ( $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ ), bentonite ( $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), aluminum silicate ( $\text{Al}_2\text{SiO}_5$ ,  $\text{Al}_4 \cdot 3\text{SiO}_4 \cdot 5\text{H}_2\text{O}$ , and so on), magnesium silicate ( $\text{Mg}_2\text{SiO}_4$ ,  $\text{MgSiO}_3$ , and so on), calcium silicate ( $\text{Ca}_2\text{SiO}_4$ , and so on), aluminum calcium silicate ( $\text{Al}_2\text{O}_3 \cdot \text{CaO} \cdot 2\text{SiO}_2$ , and so on), magnesium calcium  
20 silicate ( $\text{CaMgSiO}_4$ ), calcium carbonate ( $\text{CaCO}_3$ ), zirconium oxide ( $\text{ZrO}_2$ ), zirconium hydroxide [ $\text{ZrO}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ], zirconium carbonate [ $\text{Zr}(\text{CO}_3)_2$ ], and crystalline aluminosilicates containing charge-compensating hydrogen, alkali metal or alkaline earth metal such as various zeolites. These fillers may be used alone or in a combination  
25 of two or more. Among these fillers, the carbon black, silica, alumina, alumina hydrate, clay and calcium carbonate are preferable.

[0027] In the production of the slurry solution can be used a known method and is not particularly limited. For example, the slurry solution can be prepared by charging predetermined amounts of the  
30 filler and the water into the homomixer and agitating for a certain time. Also, a high shear mixer of rotor-stator type, a high-pressure homogenizer, an ultrasonic homogenizer, a colloid mill and so on may be used in the production of the slurry solution. For example, the

slurry solution can be prepared by charging predetermined amounts of the filler and the water into the colloid mill and then agitating at a high speed for a certain time. At this point, the concentration of the filler in the slurry solution is preferably 0.5-60 mass%, more preferably 1-30 mass%. Also, it is preferable to compound the filler in an amount of 5-100 parts by mass, more preferably 10-70 parts by mass based on 100 parts by mass of the rubber component. When the amount of the filler compounded is less than 5 parts by mass, there is a possibility that sufficient reinforcing effect cannot be obtained, while when it exceeds 100 parts by mass, there is a possibility that the processability is deteriorated.

[0028] In the production method of the invention, after the rubber solution is mixed with the filler slurry solution, the resulting mixture is coagulated. As the coagulation method is mentioned a method of adding a coagulating agent to the mixture to conduct solidification. However, the solidification may be conducted by mixing the rubber solution with the slurry solution, and in this case the addition of the coagulating agent is not necessarily required. The coagulating agent is not particularly limited, and includes an acid such as formic acid, sulfuric acid or the like, and a salt such as sodium chloride or the like. When the water-based rubber latex is used as the rubber solution, the resulting coagulated mass has usually a water content of 5-40 mass%, and is dried and used as a rubber composition or the like.

[0029] To the rubber master batch may be added additives such as a surfactant, a vulcanizing agent, an antioxidant, a colorant, a dispersant and the like, if necessary. These additives are preferable to be added to the rubber solution and/or the slurry solution prior to the mixing of the rubber solution and the slurry solution.

[0030] In the method for producing the rubber master batch according to the invention, the drying is usually performed as a final step. In the drying can be used usual dryers such as a vacuum dryer, an air dryer, a drum dryer, a band dryer and so on. In order to further improve the dispersibility and homogeneity of the filler, it is



preferable to conduct the drying while applying a mechanical shearing force. By drying while applying the mechanical shear force can be obtained a rubber having excellent processability, reinforcing effect and low fuel consumption. The drying can be carried out by a usual  
5 milling machine, but it is preferable to use a screw-type continuous milling machine from a viewpoint of the industrial productivity, and it is more preferable to use a corotating or counterrotating biaxial milling extruder. As the screw-type continuous milling machine can be used commercially available products, for example, a biaxial  
10 milling extruder made by Kobe Steel, Ltd. and so on.

[0031] The rubber composition according to the invention comprises the rubber master batch obtained by the above-described method. Since the above rubber master batch is excellent in the homogeneity, the rubber composition of the invention is also excellent in the  
15 homogeneity. To the rubber composition can be added additives usually used in the rubber industry such as a vulcanizing agent, a vulcanization accelerator, an antioxidant, a scorch retarder, zinc oxide, stearic acid and the like within a scope of not damaging the object of the invention. Furthermore, the rubber composition of the invention  
20 can be preferably used in rubber articles such as a tire and a belt.

[0032] The following examples are given in illustration of the invention and are not intended as limitations thereof.

[0033] (Comparative Example 1)

A rubber solution A is prepared by diluting a field latex of a  
25 natural rubber (pH is adjusted to 10.5 with aqueous ammonia, a content of rubber component : 27.4 mass%) with deionized water so as to adjust the content of rubber component to 20 mass%. Also, carbon black N110 is added to deionized water and dispersed in the form of a slurry by means of a homodisper [made by TOKUSHU KIKI KOGYO  
30 Co., Ltd.] to prepare a filler slurry B (a content of carbon black: 5 mass%). The rubber solution A is charged at a flow rate of 500mL/min and the filler slurry B is simultaneously charged at a flow rate of 1000mL/min into a tank provided with an impeller-type agitator

for 5 minutes with agitating. After the completion of the charge, formic acid is added with agitating to adjust pH to about 5 to complete the coagulation. The resulting coagulated mass is collected with a screen having a mesh size of 30, washed with water and dried to obtain a rubber master batch.

**[0034] (Example 1)**

The above-described rubber solution A and filler slurry B are simultaneously charged into a static mixer [made by Noritake Co., Limited, an outer diameter: 1 inch, number of elements: 12] at the same flow rate as in Comparative Example 1, and the resulting mixture is charged into the tank and then formic acid is added with agitating to adjust pH to about 5 to thereby complete the coagulation. The resulting coagulated mass is collected with the screen having the mesh size of 30, washed with water and dried to obtain a rubber master batch.

**[0035] (Example 2)**

The above-described rubber solution A and filler slurry B are simultaneously charged into a colloid mill [a diameter of a rotor: 50 mm, a clearance between a rotor and a stator: 0.7 mm] at the same flow rate as in Comparative Example 1, passed therethrough once at a revolution number of 3000 rpm and charged into the tank, and then formic acid is added with agitating to adjust pH to about 5 to thereby complete the coagulation. The resulting coagulated mass is collected with the screen having the mesh size of 30, washed with water and dried to obtain a rubber master batch.

**[0036] <Evaluation of homogeneity>**

About 1g of a sample is randomly picked from 10 points in about 600g of each of the above rubber master batches, and cut into a specimen having a size of 1 cubic mm, which is precisely weighed and placed into a crucible, and heated in an electric heating furnace at 750°C for 5 minutes to combust the rubber component. After allowing to cool, the resulting residue is precisely weighed and then the amount of the filler compounded is calculated according to the following equation (II):

Amount of the filler compounded = mass of residue / (mass before combustion - mass of residue)  $\times 100$  . . . . . (II)

An average amount of 10 samples and its standard deviation  $\sigma$  are calculated to obtain results as shown in Table 1. The smaller the

5 value of  $\sigma$ , the smaller the scattering and the better the homogeneity.

[0037] [Table 1]

	Comparative Example 1	Example 1	Example 2
n=1	54.0	50.7	50.5
n=2	57.3	50.6	48.8
n=3	49.1	50.2	49.6
n=4	53.4	49.5	49.8
n=5	50.5	51.0	49.3
n=6	58.6	49.9	49.2
n=7	48.6	49.9	48.9
n=8	56.1	50.8	50.1
n=9	51.9	50.0	49.7
n=10	55.0	50.4	50.1
Average	53.5	50.3	49.6
$\sigma$	3.4	0.5	0.6

[0038] As seen from the above, the rubber master batches of the examples are homogeneously coagulated because the scattering in the amount of the filler compounded is small and the average amount of the filler compounded is near a theoretical value, i.e. 50. On the other hand, the rubber master batch of the comparative example is large in the difference between the average amount of the filler compounded and the theoretical value and the scattering of the amount of the filler compounded and is inferior in the homogeneity.